

Report for 2004IL52G: Carbonaceous Material Fractions in Sediments and Their Effect on the Sorption and Persistence of Organic Pollutants in Small Urban Watersheds

- Conference Proceedings:
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Report Follows

Problem and Research Objectives

Particle-associated contaminants (PACs) are an important contributor to urban non-point source pollution across the Nation. PACs, which include chlorinated organic compounds, trace elements, and polycyclic aromatic hydrocarbons (PAHs), pose a threat to biota in aquatic systems and humans because many are toxic, bioaccumulative, and persistent. Since the occurrence of PACs has resulted in the impairment of thousands of streams, lakes, and reservoirs, the determination of trends (or lack of trends) in PACs is of national significance and one of the objectives of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program, which is referred to as the Reconstructed Trends National Synthesis (RTNS) Study.

Numerous researchers have relied on the analysis of cores from streambed and lake sediments to identify trends in PACs in aquatic systems, and to reconstruct water-quality histories, based on the assumption that the chemical signatures in the cores reflect historical water quality in the influent streams (e.g. Charles and Hites, 1987; Eisenreich et al., 1989). Recently, Van Metre and Mahler (2004), as part of a USGS RTNS team, investigated the extent to which the contaminant concentrations and trends recorded in sediment cores were associated with suspended sediment in influent streams. Their research results support the use of sediment cores to infer streamwater-quality histories for many contaminants, but they also indicate that in small urban watersheds, concentrations of some PACs on suspended sediment in influent streams can greatly exceed those in bed surface sediment in the downstream reservoir, and that trends may not be preserved in cores for some PACs. These observations present a problem for effective sediment monitoring and best management practices for mitigating PAC occurrence. Although the significant loss of contaminants during transport and soon after deposition has been attributed to the solubilization of some contaminants, and the solubilization and mineralization of some solid-phase carbonaceous materials (CMs), relatively little is known about the role played by CM in the transport and fate of PACs in small urban watersheds.

The overall objective of this study is to determine how CM fractions in urban reservoir sediments affect the persistence of PACs, with a focus on hydrophobic organic compounds (HOCs). The specific objectives of this work include determining the persistence of different CM fractions in sediments during suspension, sedimentation, and burial, determining the CM fractions that control the sorption and persistence of PACs in urban reservoirs, and developing a model to predict PAC sorption to urban sediments.

Methodology

This research project consists of three phases.

Phase I: Sampling and PAC analysis.

Lake Como and Lake Fosdic watersheds in Fort Worth, Texas were chosen to be urban “laboratories”. Samples of lake sediments, suspended sediments and bed sediments in influent streams, soils, street dust, and parking lot dust were collected from each watershed. All samples were split; one split is being used for the analysis of PACs (trace elements, organochlorine compounds, and PAHs) and the determination of sediment deposition time at the USGS National Water Quality Lab (NWQL), and the other split is being used for CM fractionation, characterization, and sorption in our laboratory at the University of Illinois at Urbana-Champaign (UIUC).

Phase II: Enrichment and characterization of CM fractions.

All samples except suspended sediment will be density separated with a sodium polytungstate (SPT) solution to obtain light particulate organic matter (LPOM), occluded particulate organic matter (OPOM), and the remaining heavy fraction (HFr) (Wander and Yang, 2000). Each fraction will be subject to a series of chemical and/or thermal treatment steps to obtain sub-samples

enriched in different CM fractions, such as total CM, humic acid, fulvic acid, kerogen plus black carbon, and black carbon.

Sediment and CM fractions will be quantified and characterized in several ways. Surface area will be determined by gas adsorption. CHN analysis, energy dispersive spectroscopy, and X-ray photoelectron spectroscopy will be used to determine the C, H, and O contents of the samples and sample surfaces. Surface functional groups will be analyzed with Fourier-transform infrared spectroscopy.

Phase III: Measurement and prediction of sorption isotherms for PACs

Sorption isotherms will be measured using established batch equilibrium methods (Li and Werth, 2001), with bulk sediment, soil, dust, and CM fractions of these samples, using benzo(a)pyrene (BAP) and α -chlordane (α -Chl) as sorbates. Radio-labeled BAP and α -Chl will be used to distinguish spiked sorbate from background sorbate. All isotherms will be run at 22°C.

The sorption isotherms and the surface properties characterized in Phase II will be used to develop quantitative structure-activity relationship models to predict PAC sorption in other sediments and to identify mechanisms that control the sorption and persistence of PACs in urban reservoirs.

Principal Findings and Significance

So far, we have finished the tasks in Phase I and are working on Phase II.

Cooperating with the USGS NAWQA program (RTNS team), all sampling was completed in Fort Worth, Texas, in October of 2004. Sediment cores were collected at different depth. For Lake Como, three core intervals at depths of 0-5 cm, 10-15 cm and 25-30 cm were collected. For Lake Fosdic, six samples at 5-cm intervals from the surface to a depth of 30 cm were collected. In order to determine the organic carbon (OC) profiles in the sediments, samples at 2-cm interval were also collected from both lakes, 0 – 32 cm for Lake Como and 0 – 40 cm for Lake Fosdic. Suspended sediment and bed sediment samples were collected from the corresponding influent streams of both lakes. Soil samples were collected from commercial and residential areas in each lake watershed. Dust from residential streets and sealed and unsealed commercial parking lots in each watershed were also collected.

One split of all samples is being analyzed for PAC concentration and isotope radioactivity (^{137}Cs and ^{210}Pb) by NWQL, and the other split is being treated in our laboratory. After the treatment with an excess of a 5% H_2SO_3 to remove inorganic carbon, the OC and hydrogen contents of all 2-cm sediment intervals were determined with a CE 440 CHN analyzer (Exeter Analytical, Inc., MA) in the Microanalysis Laboratory at the UIUC. The OC contents of Lake Como sediments are between 3.6 – 5.6 %, without an obvious trend. However, the OC contents of Lake Fosdic sediments are greater, and there is a significant decrease in OC contents at deeper depths (6.5 – 8.5% at the depth from 0 to 25 cm; 5.0 – 6.8% at the depth from 25 to 40 cm). The different OC contents at different depths in sediments may be correlated with different CM fractions and their properties, and may influence PAC persistence. Sediment samples at 5-cm intervals are being separated into LPOM, OPOM and HF_r fractions, with 1.6 g/cm³ SPT solution, and pulverized to ~75 μm particles for complete and fast reaction in subsequent chemical treatments.

Also, some samples were sent in small amounts for PAH extraction and petrographic analysis using the facilities at Tuebingen University in Germany, including the surface sediment samples (0-5 cm) from both lakes and the soil and dust samples from Lake Como.

References:

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